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Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Offi

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Akzo Nobel N.V.
Velperweg 76
6824 BM Arnhem
PAYS-BAS

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Hydrothermal process for the preparation of quasi-crystalline boehmite

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HYDROTHERMAL PROCESS FOR THE PREPARATION OF QUASI-CRYSTALLINE BOEHMITE

Boehmite, also called alpha-monohydrate, and its dehydrated and sintered forms are some of the most extensively used aluminium oxide-hydroxide materials. These materials are used as ceramics, abrasive materials, fire-retardants, adsorbents, catalysts, fillers in composites, etc. Also, a major portion of the commercial boehmite aluminas is used in catalytic applications such as refinery catalysts, catalysts for hydroprocessing hydrocarbon feeds, reforming catalysts, pollution control catalysts, cracking catalysts, and catalysts for the production of ethylene oxide, the production of methanol, the conversion of chlorofluorohydocarbons (CFCs), and the reduction of nitrogen oxide from exhaust gases of gas turbines.

The term "hydroprocessing" in this context encompasses all processes in which a hydrocarbon feed is reacted with hydrogen at elevated temperature and elevated pressure. These processes include hydrodesulphurisation, hydrodenitrogenation, hydrodemetallisation, hydrodearomatisation, hydro-isomerisation, hydrodewaxing, (mild) hydrocracking.

The term 'boehmite' is used in the industry to describe alumina hydrates which exhibit X-ray diffraction (XRD) patterns close to that of aluminium oxide-hydroxide [AlO(OH)]. Further, the term boehmite is generally used to describe a wide range of alumina hydrates which contain different amounts of water of hydration, have different surface areas, pore volumes, specific densities, and exhibit different thermal characteristics upon thermal treatment. Yet their XRD patterns, although they exhibit the characteristic boehmite [AlO(OH)] peaks, usually vary in their widths and can also shift in their location. The sharpness of the XRD peaks and their location have been used to indicate the degree of crystallinity, crystal size, and amount of imperfections.

Broadly, there are two categories of boehmite aluminas: quasi-crystalline boehmites (QCBs) and micro-crystalline boehmites (MCBs).

In the state of the art, quasi-crystalline boehmites are also referred to as pseudo-boehmites and gelatinous boehmites. Usually these QCBs have higher surface areas, larger pores and pore volumes, and lower specific densities than MCBs. They disperse easily in water or acids, have smaller crystal sizes than MCBs, and contain a larger number of water molecules of hydration. The extent of hydration of the QCB can have a wide range of values, for example from about 1.4 up and about 2 moles of water per mole of Al, intercalated usually orderly or otherwise between the octahedral layers. DTG (differential thermographimetry) indicates that the major amount of water is released from QCBs, compared to MCBs, at a much lower temperature. The XRD Patterns of QCBs show quite broad peaks and their half-widths (i.e. the widths of the peaks at half-maximum intensity) are indicative of the crystal sizes as well as degree of crystal perfection. Some typical commercially available QCBs are Condea Pural®, Catapal®, and Versal® products.

Microcrystalline boehmites are distinguished from the QCBs due to their high degree of crystallinity, relatively large crystal size, very low surface areas, and high densities. Contrary to the QCBs the MCBs show XRD patterns with higher peak intensities and very narrow half-widths. This is due to their relatively small number of water molecules intercalated, large crystal sizes, higher degree of crystallization of the bulk material and smaller amount of crystal imperfections. Typically, the number of water molecules intercalated can vary in the range from about 1 up to about 1.4 per mole of Al. A typical commercially available MCB is Condea's P-200 ®.

MCBs and QCBs are characterized by powder X-ray reflections. The ICDD contains entries for boehmite and confirms that reflections corresponding to the (020), (021) and (041) planes would be present. For copper radiation, such reflections would appear at 14, 28 and 38 degrees 2-theta. The exact position of the reflections depends on the extent of crystallinity and the amount of water intercalated: as the amount of intercalated water increases,

the (020) reflection moves to lower values, corresponding to greater d-spacings. Nevertheless, lines close to the above positions would be indicative of the presence of one or more types of boehmite phases.

For the purpose of this specification we define quasi-crystalline boehmites to have (020) peak widths at half-length of the maximum intensity of 1.5 or greater than 1.5° 2θ. Boehmites having a (020) peak width at half-length of the maximum intensity smaller than 1.5° 2θ are considered micro-crystalline boehmites.

Overall, the basic, characteristic differences between QCBs and MCBs involve variations in the following: 3-dimensional lattice order, sizes of the crystallites, amount of water intercalated between the octahedral layers, and degree of crystal imperfections.

In this specification, the term 'boehmite' includes both MCBs and QCBs.

Boehmites are most commonly manufactured via processes involving neutralization of aluminium salts by alkalines, acidification of aluminate salts, hydrolysis of aluminium alkoxides, reaction of aluminium metal (amalgamated) with water and rehydration of amorphous rho-alumina obtained by flash-calcining aluminium trihydrate.

The pH and the temperature of the suspension during aging are critical features in the preparation of boehmites. The crystallisation rate increases with pH and temperature. The higher the pH and temperature, the more MCB is formed; the lower the pH and temperature, the more QCB is formed.

WO 01/12554 discloses the preparation of QCB by aging aluminium alkoxide, aluminium salts, thermally treated aluminium trihydrate such as flash calcined aluminium trihydrate, and/or amorphous gel alumina at a pH below 7 and, preferably, hydrothermal conditions. The temperatures used in the Examples range between 165° and 198°C.

The formation of boehmites increases with the reaction temperature. Hence, the reaction rate under hydrothermal conditions (temperature above 100°C) is higher than under thermal conditions (temperature below 100°C). Unfortunately, however, the yield of QCB during aging under hydrothermal conditions is generally lower – in favour of MCB - than under thermal conditions at the same pH.
Hence, it is an object of the present invention to provide a hydrothermal process for the preparation of QCBs which results in higher QCB yields than a prior art process using the same temperature and pH during aging.

The present invention provides a hydrothermal process for the preparation of QCBs, which results in higher QCB yields (compared to MCB yields) than the prior art hydrothermal processes.

The process according to the invention comprises the following steps:

a) preparing an aqueous precursor mixture comprising a water-insoluble aluminium source,
b) introducing an acid into the mixture in an amount which corresponds to 0.005-5.0 times the amount of Al (in moles),
c) introducing a base into the mixture in an amount which corresponds to 0.005-5.0 times the amount of Al (in moles) , and
d) aging the mixture under hydrothermal conditions to form a quasi-crystalline boehmite.

Without being bound by theory, it is believed that by adding the acid in step b), part of the water-insoluble aluminium source dissolves and/or hydroxylates, which favors the formation of nuclei. By subsequently adding a base in step c), the pH increases, which ~~results~~ in an increased crystallisation rate of boehmite. If large amounts of nuclei are formed, the formation of boehmites with small crystallites is favored over the formation of boehmites with larger crystallites. Hence, QCB formation is favored over MCB formation.

Alumina source

Suitable water-insoluble aluminium sources for use in the process according to the present invention include aluminium trihydrate or its thermally treated form, aluminium sols, gels, amorphous alumina, and mixtures thereof. Preferably, aluminium trihydrate or its thermally treated form is used.

In the present invention aluminium trihydrate includes crystalline aluminium trihydrate (ATH), for example gibbsites provided by Reynolds Aluminium Company RH-20® or JM Huber Micral® grades. Also BOC (Bauxite Ore Concentrate), bayerite, and nordstrandite. BOC is the cheapest aluminium source. The alumina trihydrate is preferred to have a particle size ranging from 1 to 150 μm, more preferably smaller than 20 μm.

Thermally treated aluminium trihydrate includes calcined aluminium trihydrate and flash-calcined aluminium trihydrate. Calcined aluminium trihydrate is readily obtained by thermally treating aluminium trihydrate (e.g. gibbsite) at a temperature above 100°C, preferably ranging from 100° to 800°C, for a period of 15 minutes to 24 hours. In any event, the calcination temperature and time for obtaining calcined aluminium trihydrate should be sufficient to cause a measurable increase of the surface area compared to the surface area of the gibbsite as produced by the Bayer process which is generally between 30 and 50 m^2/g.

Flash-calcined aluminium trihydrate is obtained by treating aluminium trihydrate at temperatures between 800°-1000°C for very short periods of time in special industrial equipment, as is described in US 4,051,072 and US 3,222,129.

Step a)

In the process according to the invention an aqueous precursor mixture is prepared comprising one or more of the above aluminium sources. Additionally, other aluminium compounds may be added to the mixture, such seeds, and/or aluminium salts such as aluminium nitrate, aluminium chloride, aluminium chlorohydrate, and sodium aluminate. Said other aluminium sources may be soluble or insoluble in water and may be added to the

aluminium source or to the aqueous mixture separately as a solid, a solution, or a suspension.

Especially when aluminium trihydrate is used as the aluminium source, seeds are desired. Suitable seeds are the known seeds to make boehmite such as commercially available boehmites (Catapal®, Condea Versal®, P-200® etcetera), amorphous seeds, milled boehmite seeds, boehmite prepared from sodium aluminate solutions, and thermally treated aluminium trihydrate (e.g. flash-calcined aluminium trihydrate) seeds.

The process can be operated in a self-seeding mode, whereby part of the boehmite formed in chemically or mechanically treated to obtain small boehmite particles, which are then used as seed.

Step b)

Step b) of the process involves the addition of acid to the precursor mixture. Any material that can be used to decrease the pH of the precursor mixture is regarded as an acid. Suitable acids are nitric acid, sulphuric acid, hydrochloric acid, formic acid, acetic acid, nitrate (e.g ammonium nitrate, cerium nitate), polysilicic acid, oxalic acid, phosphoric acid, glycolic acid, aluminium nitrate, aluminium sulphate, and mixtures thereof.

The amount of acid introduced into the mixture is 0.005 to 5.0, preferably 0.01 to 1.5, and more preferably 0.05 to 2.0 times the amount of Al present in the precursor mixture (calculated in moles).

The desired amount of acid is preferably sufficient to lower the pH of the precursor mixture to below 7. The desired amount of acid further depends on the strength of the acid, the desired crystallinity of the boehmite, the type of aluminium source (some aluminium sources consume more acid than others), the solids content of the precursor mixture (the higher the solids content, the lower the amount of acid required to reach a certain pH), the type and amount of seeds, etc.

Step c)

The next step requires the addition of base. Any material that can be used to increase the pH of the mixture is regarded as a base.

Suitable bases are sodium hydroxide, potassium hydroxide, ammonium hydroxide, ammonium hydroxycarbonate, sodium aluminate, and mixtures thereof.

The amount of base introduced into the mixture is 0.005 to 5.0, preferably 0.01 to 1.5, and more preferably 0.05 to 2.0 times the amount of Al present in the precursor mixture (calculated in moles).

The desired amount of base added in step c), relative to the amount of Al, depends on the strength of the base, the desired end-pH and the desired type of boehmite, the type of aluminium source, the solids content of the precursor mixture, the type and amount of seeds, and the amount and strength of the acid added in step b.

It is preferred to wait, after addition of acid, for about 1-60 minutes before adding the base. During this period the mixture can be mixed, milled, and/or pre-aged.

Step d)

The precursor mixture is aged under hydrothermal conditions, i.e. in aquoues environment and at temperatures above 100°C. The aging temperature is preferably 100-250°C, more preferably 150-200°C. Aging is generally conducted for 20 minutes to 48 hours, preferably 20 minutes to 8 hours, more preferably 20 minutes to 2 hours.

If desired, one or more additives can be added to the precursor mixture, either before or during aging. Examples of such additives are compounds comprising rare earth metals (for example La and Ce), Si (e.g. silicates), P, B, group VI metals, group VIII metals, alkaline earth metals (for instance Mg, Ca, and Ba) and/or transition metals (for example Mn, Fe, Co, Ti, Zr, Cu, Ni, Zn, Mo, W, V, Sn), swellable clays like smectites and their ion-exchanged forms.

Examples of suitable smectites are montmorillonite (e.g. bentonite), beidellite, nontronite, hectorite (e.g. Laponite®), saponite, sauconite, and modified forms thereof.
Also organic additives can be added, such as polymers, surfactants, carbon, carbohydrates (sugars, starches), and other pore regulating agents.
The additives can be added to the precursor mixture as such, and/or as already present in the water-insoluble aluminium source or the optional seed, by using doped aluminium source or a doped seed. Some additives can also function as seed.

Furthermore, it is possible to mill the precursor mixture before and/or during aging. It is also possible to mill the water-insoluble aluminium source before its addition to the precursor mixture. In this specification the tem 'milling' is defined as any method that results in reduction of the particle size. Such a particle size reduction can at the same time result in the formation of reactive surfaces and/or heating of the particles. Instruments that can be used for milling include ball mills, high-shear mixers, colloid mixers, and electrical transducers that can introduce ultrasound waves into a slurry. Low-shear mixing, i.e. stirring that is performed essentially to keep the ingredients in suspension, is not regarded as 'milling'.

The process is preferably conducted in a continuous fashion. More preferably, this is done in an apparatus comprising two or more conversion vessels.
For example, the precursor mixture is prepared in a feed preparation vessel, whereafter the mixture is continuously pumped through two or more conversion vessels. The acid can be added to the mixture in the feed preparation vessel, or in one of the conversion vessels. Base is added in a subsequent conversion vessel.
Additives, if so desired, can be added to the mixture in any of the conversion vessels.
Each of the vessels can be adjusted to its own desirable temperature.
The total average residence time in all vessels together is preferably between 20 and 120 minutes.

If so desired, the QCB obtained can be shaped into shaped quasi-crystalline boehmite bodies, optionally with the help of binders and/or fillers. In order to obtain shaped boehmite bodies it is also possible to use a shaped water-insoluble aluminium source.
Suitable shaping methods include spray-drying, pelletising, granulating, extruding (optionally combined with kneading), beading, or any other conventional shaping method used in the catalyst and absorbent fields or combinations thereof. In case of beading or kneading it is also possible to combine the aging and shaping step and to add additives during the combined shaping and aging step.
The amount of liquid present in the mixture to be shaped should be adapted to the specific shaping step to be conducted. It might be advisable to partially remove the liquid used in the precursor mixture and/or add an additional or another liquid, and/or to change the pH of the aged mixture to make the mixture gellable and thus suitable for shaping. Additives commonly used in the different shaping methods, e.g. extrusion additives, may be added to the mixture.

The QCB prepared according to the process of the invention is extremely suitable as component or starting material for catalyst compositions or catalyst additives. To this end the boehmite is combined with, e.g., binders, fillers (e.g. clay such as kaolin, titanium oxide, zirconia, silica, silica-alumina, bentonite, etcetera), catalytically active material such as molecular sieves (e.g. ZSM-5, zeolite Y, USY REY, and RE-USY zeolite, zeolite beta, mordenite, MCM-type materials), and any other catalyst components (e.g. pore regulating additives) which are commonly used in catalyst compositions.
Furthermore, the boehmite may be mixed with other metal oxides or hydroxides, binders, fillers, extenders, activators, pore regulating additives, etc., to produce absorbents, ceramics, substrates, or carriers.

The so-prepared boehmite can suitably be used, optionally after calcination, in refinery catalysts, catalysts for hydroprocessing (hydrdesulfurisation,

hydrodenitrogenation, hydrodemetallisation) hydrocarbon feeds, reforming catalysts, FCC catalysts or additives, Fisher-Tropsch catalysts, hydrogenation catalysts, dehydrogenation catalysts, catalysts for the production of ethylene oxide, catalysts for the production of methanol, catalysts for the conversion of chlorofluorohydocarbons (CFCs), etc.

EXAMPLES

Comparative Example 1

Gibbsite (Huber Micral 916) [16.4 g] and flash-calcined gibbsite (Alcoa Cp-3) [4.79 g] were slurried in deionized water. The solids content of the resulting precursor mixture was about 12 wt%. After the slurry was high shear mixed, the final pH was 9.5. The resulting slurry was homogenized and aged at 185°C for two hours in an autoclave at autogeneous pressure. Subsequently, the slurry was filtered, washed and dried 120°C. X-ray diffraction analysis indicated the product consisted of MCB type of alumina.

Example 2

Gibbsite (Huber Micral 916) [16.4 g] and flash-calcined gibbsite (Alcoa Cp-3) [4.79 g] were slurried in deionized water. The solids content of the resulting precursor mixture was about 12 wt%. To this mixture, 2.70 g of a 49.0% sulfuric acid solution was added to the precursor mixture under high shear mixing [acid/Al = 0.046]. The pH of the resulting slurry was 1.77. Subsequently, 4.70 g of a 29.9% sodium hydroxide solution was added until the pH was 9.6 [base/Al = 0.12]. The resulting slurry was homogenized and aged at 185°C for two hours in an autoclave at autogeneous pressure. Subsequently the slurry was filtered, washed with dilute ammonium hydroxide solution and dried 120°C. X-ray diffraction analysis indicated the product consisted of QCB type of alumina.

Example 3

Flash-calcined gibbsite (Alcoa Cp-3) [15.9 g] was slurried in deionized water. The solids content of the resulting precursor mixture was about 12 wt%. To

this mixture, 6.00 g of a 49.0 wt% sulfuric acid solution was added to the precursor mixture under high shear mixing [acid/Al = 0.10]. The pH of the resulting slurry was 1.19. Subsequently, 4.20 g of a 29.9 wt% ammonium hydroxide solution was added until the pH was 4.48. The resulting slurry was homogenized and aged at 165°C for two hours in an autoclave at autogeneous pressure. Subsequently the slurry was filtered, washed with dilute ammonium hydroxide solution and dried 120°C. X-ray diffraction analysis indicated the product consisted of QCB type of alumina.

Example 4

Flash-calcined gibbsite (Alcoa Cp-3) [15.9 g] was slurried in deionized water. The solids content of the resulting precursor mixture was about 12 wt%. To this mixture, 4.50 g of a 49.0% sulfuric acid solution was added to the precursor mixture under high shear mixing [acid/Al = 0.077]. The pH of the resulting slurry was 1.12. Subsequently, 38.9 g of a 3.85% sodium hydroxide solution was added until the pH was 4.48. The resulting slurry was homogenized and aged at 165°C for two hours in an autoclave at autogeneous pressure. Subsequently the slurry was filtered, washed with dilute ammonium hydroxide solution and dried 120°C. X-ray diffraction analysis indicated the product consisted of QCB type of alumina.

Example 5

Flash-calcined gibbsite (Alcoa Cp-3) [13.5 g] and Catapal A [3.13 g] were slurried in deionized water. The solids content of the resulting precursor mixture was about 12 wt%. To this mixture, 7.00 g of a 35.0% nitric acid solution was added to the precursor mixture under high shear mixing [acid/Al = 0.132]. The pH of the resulting slurry was 1.20. Subsequently, 3.90 g of a 29.9% ammonium hydroxide solution was added until the pH was 5.00. The resulting slurry was homogenized and aged at 165°C for two hours in an autoclave at autogeneous pressure. Subsequently the slurry was filtered, washed and dried 120°C. X-ray diffraction analysis indicated the product consisted of QCB type of alumina.

Example 6

Flash-calcined gibbsite (Alcoa Cp-3) [15.9 g] was slurried in deionized water. The solids content of the resulting precursor mixture was about 12 wt%. To this mixture, 1.50 g of a 35.0% nitric acid solution was added to the precursor mixture under high shear mixing [acid/Al = 0.028]. The pH of the resulting slurry was 3.72. A solution consisting of 3.78 g of cerium nitrate (10% CeO_2 based on Al_2O_3) dissolved water was added to the precursor mixture as under high shear mixing. The pH of the resulting slurry was 3.06. Subsequently, 0.40 g of a 29.9% ammonium hydroxide solution was added until the pH was 4.50. The resulting slurry was homogenized and aged at 165°C for two hours in an autoclave at autogeneous pressure. Subsequently the slurry was filtered, washed and dried 120°C. X-ray diffraction analysis indicated the product consisted of QCB type of alumina.

Example 7

Flash-calcined gibbsite (Alcoa Cp-3) [15.9 g] was slurried in deionized water. The solids content of the resulting precursor mixture was about 12 wt%. To this mixture, 5.30 g of a 49.0% sulfuric acid solution was added to the precursor mixture under high shear mixing [acid/Al = 0.164]. The pH of the resulting slurry was 2.15. Subsequently, 13.70 g of a 29.9% ammonium hydroxide solution was added until the pH was 9.54. The resulting slurry was homogenized and aged at 165°C for two hours in an autoclave at autogeneous pressure. Subsequently the slurry was filtered, washed and dried 120°C. X-ray diffraction analysis indicated the product consisted of QCB type of alumina.

Example 8

Gibbsite (Huber Micral 916) [23.4 g] was slurried in deionized water. The solids content of the resulting precursor mixture was about 12 wt%. To this precursor mixture, 1.70 g of a 35.0% nitric acid solution was added and milled in a colloidal mill [acid/Al = 0.045]. The pH of the resulting slurry was 1.85. Subsequently, 1.00 g of a 29.9% ammonium hydroxide solution was added until the pH was 4.99. The resulting slurry was homogenized and aged at

185°C for two hours in an autoclave at autogeneous pressure. Subsequently the slurry was filtered, washed and dried 120°C. X-ray diffraction analysis indicated the product consisted of QCB type of alumina.

Example 9

Gibbsite (Huber Micral 916) [23.4 g] was slurried in deionized water. The solids content of the resulting precursor mixture was about 12 wt%. To this precursor mixture, 1.40 g of a 49.0 % sulfuric acid solution was added and the resulting mixture was milled in a colloidal mill [acid/Al = 0.045]. The pH of the resulting slurry was 1.85. Subsequently, 3.40 g of a 29.9% ammonium hydroxide solution was added until the pH was 9.55. The resulting slurry was homogenized and aged at 185°C for two hours in an autoclave at autogeneous pressure. Subsequently the slurry was filtered, washed and dried 120°C. X-ray diffraction analysis indicated the product consisted of QCB type of alumina.

Example 10

Gibbsite (Huber Micral 916) [16.4 g] and flash-calcined gibbsite (Alcoa Cp-3) [4.79 g] were slurried in deionized water. The solids content of the resulting precursor mixture was about 12 wt%. To this mixture, 2.30 g of a 35.0% nitric acid solution was added to the precursor mixture under high shear mixing [acid/Al = 0.043]. The pH of the resulting slurry was 1.91. Subsequently, 1.60 g of a 29.9% ammonium hydroxide solution was added until the pH was 5.04. The resulting slurry was dispersed in a colloidal and aged at 185°C for two hours in an autoclave at autogeneous pressure. Subsequently the slurry was filtered, washed and dried 120°C. X-ray diffraction analysis indicated the product consisted of QCB type of alumina.

Example 11

Gibbsite (Huber Micral 916) [16.4 g] and Catapal A [6.25 g] were slurried in deionized water. The solids content of the resulting precursor mixture was about 12 wt%. To this mixture, 2.60 g of a 35.0% nitric acid solution was added to the precursor mixture under high shear mixing [acid/Al = 0.049]. The

pH of the resulting slurry was 1.84. Subsequently, 1.30 g of a 29.9% ammonium hydroxide solution was added until the pH was 4.96. The resulting slurry was dispersed in a colloidal mill and aged at 185°C for two hours in an autoclave at autogeneous pressure. Subsequently the slurry was filtered, washed and dried 120°C. X-ray diffraction analysis indicated the product consisted of QCB type of alumina.

Example 12

Gibbsite (Huber Micral 916) [16.4 g] and Catapal A [6.25 g] were slurried in deionized water. The solids content of the resulting precursor mixture was about 12 wt%. To this mixture, 2.10 g of a 49.0 % sulfuric acid solution was added to the precursor mixture under high shear mixing [acid/Al = 0.049]. The pH of the resulting slurry was 1.84. Subsequently, 6.70 g of a 29.9% ammonium hydroxide solution was added until the pH was 9.55. The resulting slurry was dispersed in a colloidal mill and aged at 185°C for two hours in an autoclave at autogeneous pressure. Subsequently the slurry was filtered, washed and dried 120°C. X-ray diffraction analysis indicated the product consisted of QCB type of alumina.

Example 13

Gibbsite (Huber Micral 916) [16.4 g] and flash-calcined gibbsite (Alcoa Cp-3) [4.79 g] were slurried in deionized water. The solids content of the resulting precursor mixture was about 12 wt%. To this mixture, 2.80 g of a 35.0% nitric acid solution was added to the precursor mixture under high shear mixing [acid/Al = 0.053]. The pH of the resulting slurry was 1.83. To this mixture, 6.20 g of a 28.54% sodium silicate solution (6% SiO_2 based on total Al_2O_3) was added. The pH of the resulting slurry was 3.42. Subsequently, 0.50 g of a 29.9% ammonium hydroxide solution was added until the pH was 5.25. The resulting slurry was homogenized and aged at 185°C for two hours in an autoclave at autogeneous pressure. Subsequently the slurry was filtered, washed and dried 120°C. X-ray diffraction analysis indicated the product consisted of QCB type of alumina.

Example 14

Gibbsite (Huber Micral 916) [16.4 g] and flash-calcined gibbsite (Alcoa Cp-3) [4.79 g] were slurried in deionized water. The solids content of the resulting precursor mixture was about 12 wt%. To this mixture, 2.80 g of a 35.0% nitric acid solution was added to the precursor mixture under high shear mixing [acid/Al = 0.053]. The pH of the resulting slurry was 1.83. To this mixture, 6.20 g of a 28.54% sodium silicate solution (6% SiO_2 based on total Al_2O_3) was added. The pH of the resulting slurry was 3.42. Subsequently, 2.60 g of a 29.9% ammonium hydroxide solution was added until the pH was 9.54. The resulting slurry was homogenized and aged at 185°C for two hours in an autoclave at autogeneous pressure. Subsequently the slurry was filtered, washed and dried 120°C. X-ray diffraction analysis indicated the product consisted of QCB type of alumina.

Example 15

Gibbsite (Huber Micral 916) [16.4 g] and flash-calcined gibbsite (Alcoa Cp-3) [4.79 g] were slurried in deionized water. The solids content of the resulting precursor mixture was about 12 wt%. To this mixture, 3.20 g of a 35.0% nitric acid solution was added to the precursor mixture under high shear mixing [acid/Al = 0.060]. The pH of the resulting slurry was 1.81. To this mixture, 8.90 g of a 13.34% sodium phosphate solution (3.4% P_2O_5 based on total Al_2O_3) was added. The pH of the resulting slurry was 4.98. The resulting slurry was homogenized and aged at 185°C for two hours in an autoclave at autogeneous pressure. Subsequently the slurry was filtered, washed and dried 120°C. X-ray diffraction analysis indicated the product consisted of QCB type of alumina.

Example 16

Gibbsite (Huber Micral 916) [16.4 g] and flash-calcined gibbsite (Alcoa Cp-3) [4.79 g] were slurried in deionized water. The solids content of the resulting precursor mixture was about 12 wt%. To this mixture, 3.20 g of a 35.0% nitric acid solution was added to the precursor mixture under high shear mixing [acid/Al = 0.060]. The pH of the resulting slurry was 1.81. To this mixture,

8.90 g of a 13.34% sodium phosphate solution (3.4% P_2O_5 based on total Al_2O_3) was added. The pH of the resulting slurry was 4.98. Subsequently, 2.70 g of a 29.9% ammonium hydroxide solution was added until the pH was 9.50. The resulting slurry was homogenized and aged at 185°C for two hours in an autoclave at autogeneous pressure. Subsequently the slurry was filtered, washed and dried 120°C. X-ray diffraction analysis indicated the product consisted of QCB type of alumina.

Example 17

Gibbsite (Huber Micral 916) [16.4 g] and flash-calcined gibbsite (Alcoa Cp-3) [4.79 g] were slurried in deionized water. The solids content of the resulting precursor mixture was about 12 wt%. To this mixture, 3.20 g of a 35.0% nitric acid solution was added to the precursor mixture under high shear mixing [acid/Al = 0.060]. The pH of the resulting slurry was 1.55. . To this mixture, 3.1 g of a 28.54% sodium silicate solution (3% SiO2 based on total Al2O3) was added. The pH of the resulting slurry was 2.56. Finally, to this mixture, 6.8 g of a 13.34% sodium phosphate solution (2.6% P_2O_5 based on total Al_2O_3) was added. The resulting slurry was homogenized and aged at 185°C for two hours in an autoclave at autogeneous pressure. Subsequently the slurry was filtered, washed and dried 120°C. X-ray diffraction analysis indicated the product consisted of QCB type of alumina.

Example 18

Gibbsite (Huber Micral 916) [16.4 g] and flash-calcined gibbsite (Alcoa Cp-3) [4.79 g] were slurried in deionized water. The solids content of the resulting precursor mixture was about 12 wt%. To this mixture, 3.20 g of a 35.0% nitric acid solution was added to the precursor mixture under high shear mixing [acid/Al = 0.060]. The pH of ~~the resulting~~ slurry was 1.55. . To this mixture, 3.1 g of a 28.54% sodium silicate solution (3% SiO2 based on total Al2O3) was added. The pH of the resulting slurry was 2.56. Finally, to this mixture, 6.8 g of a 13.34% sodium phosphate solution (2.6% P_2O_5 based on total Al_2O_3) was added. The pH of the resulting slurry was 4.99. Subsequently, 3.3 g of a 29.9% ammonium hydroxide solution was added until the pH was 9.53.

The resulting slurry was homogenized and aged at 185°C for two hours in an autoclave at autogeneous pressure. Subsequently the slurry was filtered, washed and dried 120°C. X-ray diffraction analysis indicated the product consisted of QCB type of alumina.

Example 19

Flash-calcined gibbsite (Alcoa Cp-3) [16.4 g] was slurried in deionized water. The solids content of the resulting precursor mixture was about 12 wt%. To this mixture, 23.0 g of a 14.90% sodium aluminate solution was added. The Al_2O_3 weight ratio resulting from flash-calcined to sodium aluminate was 85:15. The pH of the resulting slurry was 13.2. To this mixture, 41.4 g of a 35.0% nitric acid solution was added to the precursor mixture under high shear mixing [acid/Al = 0.950]. The pH of the resulting slurry was 1.64. Subsequently, 4.5 g of a 29.9% ammonium hydroxide solution was added until the pH was 5.40. The resulting slurry was homogenized and aged at 165°C for two hours in an autoclave at autogeneous pressure. Subsequently the slurry was filtered, washed and dried 120°C. X-ray diffraction analysis indicated the product consisted of QCB type of alumina.

Example 20

Gibbsite (Huber Micral 916) [16.4 g] and flash-calcined gibbsite (Alcoa Cp-3) [4.79 g] were slurried in deionized water. The solids content of the resulting precursor mixture was about 12 wt%. To this mixture, 2.10 g of a 49.0% sulfuric acid solution was added to the precursor mixture under high shear mixing [acid/Al = 0.036]. The pH of the resulting slurry was 1.88. Subsequently, 1.40 g of magnesium hydroxide was added until the pH was 6.30. The resulting slurry was homogenized and aged at 185°C for two hours in an autoclave at autogeneous pressure. Subsequently the slurry was filtered, washed and dried 120°C. X-ray diffraction analysis indicated the product consisted of QCB type of alumina.

Example 21

Gibbsite (Huber Micral 916) [16.4 g] and flash-calcined gibbsite (Alcoa Cp-3) [4.79 g] were slurried in deionized water. The solids content of the resulting precursor mixture was about 12 wt%. To this mixture, 2.10 g of a 30.0% monoammonium hydrogen phosphate solution was added to the precursor mixture under high shear mixing. The pH of the resulting slurry was 5.54. Subsequently, 2.36 g of a 10.4% tetra sodium pyrophoshate solution and 5.50 g of a 3.85% sodium hydroxide solution was added until the pH was 7.98. The resulting slurry was homogenized and aged at 185°C for two hours in an autoclave at autogeneous pressure. Subsequently the slurry was filtered, washed and dried 120°C. X-ray diffraction analysis indicated the product consisted of QCB type of alumina.

Example 22

Gibbsite (Huber Micral 916) [16.4 g] and flash-calcined gibbsite (Alcoa Cp-3) [4.79 g] were slurried in deionized water. The solids content of the resulting precursor mixture was about 12 wt%. To this mixture, 0.30 g of a 49.0% sulfuric acid solution was added to the precursor mixture under high shear mixing [acid/Al = 0.0051]. The pH of the resulting slurry was 5.15. Subsequently, 4.17 g of a 10.4% tetrasodium pyrophoshate solution (1.0% P_2O_5 based on total Al_2O_3) and 0.70 g of a 3.85% sodium hydroxide solution was added until the pH was 9.37. The resulting slurry was homogenized and aged at 185°C for two hours in an autoclave at autogeneous pressure. Subsequently the slurry was filtered, washed and dried 120°C. X-ray diffraction analysis indicated the product consisted of QCB type of alumina.

Example 23

Gibbsite (Huber Micral 916) [16.4 g] and flash-calcined gibbsite (Alcoa Cp-3) [4.79 g] were slurried in deionized water. The solids content of the resulting precursor mixture was about 12 wt%. To this mixture, 0.30 g of a 49.0% sulfuric acid solution was added to the precursor mixture under high shear mixing [acid/Al = 0.0051]. The pH of the resulting slurry was 5.15. Subsequently, 2.00 g of a 19.0% sodium metasilicate solution (2.2% SiO_2

based on total Al_2O_3) and 2.36 g of a 10.4% tetrasodium pyrophosphate solution (2.0% P_2O_5 based on the total Al_2O_3) was added until the pH was 9.37. The resulting slurry was homogenized and aged at 185°C for two hours in an autoclave at autogeneous pressure. Subsequently the slurry was filtered, washed and dried 120°C. X-ray diffraction analysis indicated the product consisted of QCB type of alumina.

Example 24

Gibbsite (Huber Micral 916) [16.4 g] and flash-calcined gibbsite (Alcoa Cp-3) [4.79 g] were slurried in deionized water. The solids content of the resulting precursor mixture was about 12 wt%. To this mixture, 0.30 g of a 49.0% sulfuric acid solution was added to the precursor mixture under high shear mixing [acid/Al = 0.0051]. The pH of the resulting slurry was 5.15. Subsequently, 3.75 g of a 14.9% sodium aluminate solution was added to increase the pH in the range of 10-11. The resulting slurry was homogenized and aged at 185°C for two hours in an autoclave at autogeneous pressure. Subsequently the slurry was filtered, washed and dried 120°C. X-ray diffraction analysis indicated the product consisted of QCB type of alumina.

Example 25

Gibbsite (Huber Micral 916) [16.4 g] and flash-calcined gibbsite (Alcoa Cp-3) [4.79 g] were slurried in deionized water. The solids content of the resulting precursor mixture was about 12 wt%. To this mixture, 2.80 g of a 26.8% aluminium sulfate solution was added to the precursor mixture under high shear mixing. The pH of the resulting slurry was 4.03. Subsequently, 5.00 g of a 19.0% sodium metasilicate solution resulting in a final pH of 9.1. The resulting slurry was homogenized and aged at 185°C for two hours in an autoclave at autogeneous pressure. Subsequently the slurry was filtered, washed with dilute ammonium hydroxide solution and dried 120°C. X-ray diffraction analysis indicated the product consisted of QCB type of alumina.

Example 26

Gibbsite (Huber Micral 916) [16.4 g] and flash-calcined gibbsite (Alcoa Cp-3) [4.79 g] were slurried in deionized water. The solids content of the resulting precursor mixture was about 12 wt%. To this mixture, 5.00 g of a 6.0% freshly prepared polysilisic acid (2.0% SiO_2 based on the total Al_2O_3) was added to the precursor mixture under high shear mixing. The pH of the resulting slurry was 1.9. Subsequently, 4.7 g of a 30.0% ammonium hydroxide was added resulting in a final pH of 9.5. The resulting slurry was homogenized and aged at 185°C for two hours in an autoclave at autogeneous pressure. Subsequently the slurry was filtered, washed and dried 120°C. X-ray diffraction analysis indicated the product consisted of QCB type of alumina.

Comparative Example 27

Gibbsite (Huber Micral 916) [16.4 g] and flash-calcined gibbsite (Alcoa Cp-3) [4.79 g] were slurried in deionized water. The solids content of the resulting precursor mixture was about 12 wt%. After the slurry was high shear mixed the final pH was 9.5. Subsequently, 0.3 g of a 29.9% sodium hydroxide solution was added until the pH was 11. The resulting slurry was homogenized and aged at 185°C for two hours in an autoclave at autogeneous pressure. Subsequently the slurry was filtered, washed with dilute ammonium hydroxide solution and dried 120°C. X-ray diffraction analysis indicated the product consisted of MCB type of alumina.

Comparative Example 28

Flash-calcined gibbsite (Alcoa Cp-3) [15.9 g] was slurried in deionized water. The solids content of the resulting precursor mixture was about 12 wt%. The pH of the resulting slurry was 9.7. Subsequently, 0.35 g of a 29.9% sodium hydroxide solution was added until the pH was 11. The resulting slurry was homogenized and aged at 185°C for two hours in an autoclave at autogeneous pressure. Subsequently the slurry was filtered, washed with dilute ammonium hydroxide solution and dried 120°C. X-ray diffraction analysis indicated the product consisted of MCB type of alumina.

Comparative Example 29

Flash-calcined gibbsite (Alcoa Cp-3) [15.9 g] was slurried in deionized water. The solids content of the resulting precursor mixture was about 12 wt%. To this mixture, 3.9 g of a 49.0% sulfuric acid solution was added to the precursor mixture under high shear mixing [acid/Al = 0.066]. The pH of the resulting slurry was 1.5. The resulting slurry was homogenized and aged at 165°C for two hours in an autoclave at autogeneous pressure. Subsequently the slurry was filtered, washed with dilute ammonium hydroxide solution and dried 120°C. X-ray diffraction analysis indicated the product contained a small amount of poor crystalline QCB type of alumina.

Example 30

Flash-calcined gibbsite (Alcoa Cp-3) [15.9 g] was slurried in deionized water. The solids content of the resulting precursor mixture was about 12 wt%. To this mixture, 21.9 g of a 15.0% zinc nitrate solution and 4.2 g of a 35.0% nitric acid solution were added to the precursor mixture under high shear mixing. The pH of the resulting slurry was 2.2. Subsequently, 2.50 g of a 29.9% ammonium hydroxide solution was added until the pH was 5.50. The resulting slurry was homogenized and aged at 185°C for two hours in an autoclave at autogeneous pressure. Subsequently the slurry was filtered, washed and dried 120°C. X-ray diffraction analysis indicated the product consisted of QCB type of alumina.

Example 31

Flash-calcined gibbsite (Alcoa Cp-3) [15.9 g] was slurried in deionized water. The solids content of the resulting precursor mixture was about 12 wt%. To this mixture, 4.0 g of a 20.0% vanadyl sulfate solution and 5.2 g of a 49.0% sulfuric acid solution were added to the precursor mixture under high shear mixing. The pH of the resulting slurry was 2.5. Subsequently, 3.0 g of a 29.9% ammonium hydroxide solution was added until the pH was 7.50. The resulting slurry was homogenized and aged at 185°C for two hours in an autoclave at autogeneous pressure. Subsequently the slurry was filtered,

washed and dried 120°C. X-ray diffraction analysis indicated the product consisted of QCB type of alumina.

Example 32

Flash-calcined gibbsite (Alcoa Cp-3) [15.9 g] was slurried in deionized water. The solids content of the resulting precursor mixture was about 12 wt%. To this mixture, 8.9 g of a 20.0% magnesium sulfate solution and 5.0 g of a 49.0% sulfuric acid solution were added to the precursor mixture under high shear mixing. The pH of the resulting slurry was 2.3. Subsequently, 5.9 g of a 29.9% ammonium hydroxide solution was added until the pH was 8.0. The resulting slurry was homogenized and aged at 185°C for two hours in an autoclave at autogeneous pressure. Subsequently the slurry was filtered, washed with dilute ammonium hydroxide solution and dried 120°C. X-ray diffraction analysis indicated the product consisted of QCB type of alumina.

Comparative Example 33

Flash-calcined gibbsite (Alcoa Cp-3) [32.0 g] was slurried in deionized water. The solids content of the resulting precursor mixture was about 12 wt%. To this mixture, 3.0 g of a 49.0% sulfuric acid solution was added to the precursor mixture under high shear mixing [acid/Al = 0.024]. The pH of the resulting slurry was 3.6.

The resulting slurry was divided into two portions. The first portion was aged at 165°C for two hours, while the second portion was aged at 185°C for one hour in an autoclave at autogeneous pressure. After aging these slurries were filtered, washed with dilute ammonium hydroxide solution and dried 120°C. X-ray diffraction analysis indicated that these products contained substantial amounts of unconverted Boehmite alumina and only a small amount of QCB type alumina.

Example 34

Comparative Example 33 was repeated except that after the addition of sulfuric acid that produced a pH of 3.6, ammonium hydroxide [18.5 g of 29.9% solution was added to increase the pH to about 8.5 with high shear mixing.

The resulting slurry was divided into two portions. The first portion was aged at 165°C for two hours, while the second portion was aged at 185°C for one hour in an autoclave at autogeneous pressure. After aging these slurries were filtered, washed with dilute ammonium hydroxide solution and dried 120°C. X-ray diffraction analysis indicated that both products were QCB type alumina.

Comparative Example 35

Flash-calcined gibbsite (Alcoa Cp-3) [15.9 g] was slurried in deionized water. The solids content of the resulting precursor mixture was about 12 wt%. After the slurry was high shear mixed the final pH was 9.7. The resulting slurry was homogenized and aged at 185°C for two hours in an autoclave at autogeneous pressure. Subsequently the slurry was filtered, washed and dried 120°C. X-ray diffraction analysis indicated the product consisted of MCB type of alumina.

Example 36

Flash-calcined gibbsite (Alcoa Cp-3) [32.0 g] was slurried in deionized water. The solids content of the resulting precursor mixture was about 12 wt%. To this mixture, 9.40 g of a 49.0% sulfuric acid solution was added to the precursor mixture under high shear mixing [acid/Al = 0.075]. The pH of the resulting slurry was about 1.2. Subsequently, 23.8 g of 29.9% sodium hydroxide solution was added with high shear mixing resulting in a final pH of about 9.8.

The resulting slurry was divided into two portions. The first portion was aged at 165°C for two hours, while the second portion was aged at 185°C for one hour in an autoclave at autogeneous pressure. After aging these slurries were filtered, washed with dilute ammonium hydroxide solution and dried 120°C. X-ray diffraction analysis indicated that both products were QCB type alumina.

CLAIMS

1. Process for the preparation of quasi-crystalline boehmite comprising the steps of:
   a) preparing an aqueous precursor mixture comprising a water-insoluble aluminium source,
   b) introducing an acid into the mixture in an amount which corresponds to 0.005-5.0 times the amount of Al (in moles),
   c) introducing a base into the mixture in an amount which corresponds to 0.005-5.0 times the amount of Al (in moles) , and
   d) aging the mixture under hydrothermal conditions to form a quasi-crystalline boehmite.

2. Process according to claim 1 wherein the amount of acid introduced in step b) corresponds to 0.05-2.0 times the amount of Al.

3. Process according to claim 1 or 2 wherein the amount of base introduced in step c) corresponds to 0.05-2.0 times the amount of Al.

4. Process according to any one of the preceding claims wherein the water-insoluble aluminium source is selected from the group consisting of aluminium trihydrate, thermally treated aluminium trihydrate, aluminium sol, aluminium gel, and mixtures thereof.

5. Process according to any one of the preceding claims wherein the water-insoluble aluminium source and/or the precursor mixture is/are milled.

6. Process according to any one of the preceding claims followed by shaping the formed quasi-crystalline boehmite into shaped bodies.

7. Process according to any one of the preceding claims wherein additives are added either before or during step d).

8. Process according to any one of the preceding claims wherein the process is conducted in a continuous mode in one or more vessels.

9. Process according to claim 8 wherein the process in conducted in at least two vessels.

10. Process according to claim 8 or 9 wherein the total average residence time in all vessels together is between 20 and 120 minutes.

ABSTRACT

Process for the preparation of quasi-crystalline boehmite comprising the steps of:

a) preparing an aqueous precursor mixture comprising a water-insoluble aluminium source,

b) introducing an acid into the mixture in an amount which corresponds to 0.005-5.0 times the amount of Al (in moles),

c) introducing a base into the mixture in an amount which corresponds to 0.005-5.0 times the amount of Al (in moles) , and

d) aging the mixture under hydrothermal conditions to form a quasi-crystalline boehmite.

This process provides for the hydrothermal preparation of quasi-crystalline boehmites with increased yield of quasi-crystalline boehmite.

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